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Electronically excited C_2 from laser photodissociated C_{60}

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Abstract

Spectral and transient emission measurements are made of radiation from products of laser excitation of buckminsterfullerene (C_{60}) vapor diluted in argon at 973 K. The principal radiation is from the Swan band system of C_2 and, at early times, also from a black-body continuum. Transient measurements indicate two characteristic periods of decay 2 and 50 μs long, with characteristic decay times of ~0.3 and 5 μs, respectively. The first period is thought to be associated with decomposition and radiative cooling of C_{60} molecules or nano-sized carbon particles and the second period continues with decomposition products of laser excited C_{60}, C_{58}, C_{56}, etc. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

It is speculated that fullerenes are possible precursors to the formation of single-wall carbon nanotubes using the laser ablation process [1]. However, the existence of fullerenes is difficult to show directly since C_{60} molecules in the gas phase do not have a strong characteristic visible emission spectrum. In the laser ablation process, the main radiation observed is that of C_2 Swan bands [2,3]. Arepalli and Scott [1] observed that C_2 Swan band radiation persists for an unusually long period after the laser pulse. Its characteristic decay time is on the order of 8–27 μs, while the natural lifetime of the $d^3\Pi_g$-state of C_2 is only ~100 ns. Therefore, excited C_2 must continue to be created after the initial laser pulse; and whatever produces it must have a long lifetime. In the laser ablation process, a target of graphite containing a few percent of Ni and Co is irradiated by laser pulses of 532 and 1064 nm. These 1.5 J/cm^2 laser pulses, separated by ~50 ns, heat the surface to several thousand degrees and cause the target to ablate. Most of the ablation product is C_3; but some C_2, and possibly some atomic C are also produced. The lifetime of C is very short and within a few tens of nanoseconds recombines to form higher-molecular-weight carbon molecules. However, C may be produced from exchange reactions involving C_2, C_3, etc. Chemiluminescent decay of C_2 formed from recombination of C would be completed very quickly – much faster than is observed in the Swan band emission decay. Therefore, another explanation of the persistent C_2 radiation must be found.

It has been known for a number of years [4–6] that the C_2 molecule is the major dissociation prod-

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uct of fullerenes excited by lasers. Photodissociation of fullerenes has been observed with mass spectrometry when C_{60} and other fullerenes are illuminated with high-intensity laser light [4]. A whole manifold of C_n molecules ($n < 60$) has been observed from photofragmentation of C_{60}. The C_{60} molecule may absorb several photons of UV or visible light, putting it in a highly vibrationally excited state. This state is unstable and results in decomposition into C_{58} and C_2. Further, C_{58} may absorb photons and decompose into smaller cage molecules, likewise by giving up C_2 molecules (the 'shrink-wrap' mechanism [7]). If the original C_{60} had sufficient excitation energy, then the C_{58} may also be excited sufficiently to dissociate by ejecting a C_2, and so on. It was tacitly assumed that the formed C_2 was in its ground state. Fullerenes have been found in abundance in the product of laser ablation of pure graphite [8,9], and have been found as an impurity in laser ablation production of single-wall carbon nanotubes. These facts lead us to expect that laser excitation of fullerenes may result in the formation of *electronically excited* C_2 molecules leading to Swan band emission. The objective of this work, then, is to investigate C_{60} excitation by lasers and the plausibility that photodissociation of fullerenes produces C_2 in electronically excited states.

2. Experiment

Measurements of the afterglow of C_{60} vapor were made in the same apparatus used for making carbon

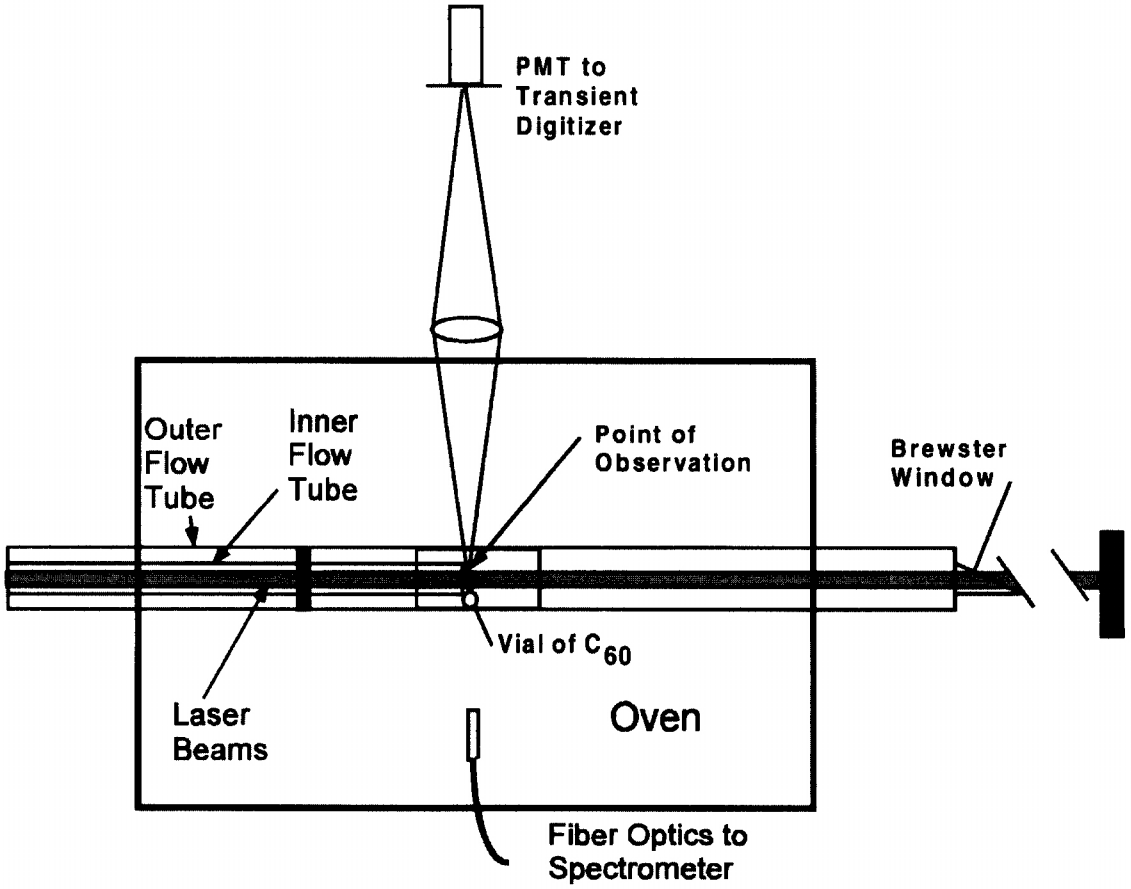

Fig. 1. Schematic of experimental configuration for laser irradiation of C_{60} inside the carbon nanotube production setup.

nanotubes by the laser ablation process at NASA Johnson Space Center [1]. The laser ablation apparatus is similar to the one used at Rice University [10], and is described in detail elsewhere [11]. The modified apparatus used for the present experiments is shown in Fig. 1. Laser beams are directed along the axis of a 56 mm diameter fused quartz tube that rests inside a tube furnace. A small vial of C_{60} powder (99.9% pure, FOMA International) was placed inside the tube near the observation ports, where the graphite target is normally placed for nanotube production. A slow argon purge flows past the vial and carries C_{60} vapor downstream, parallel to the laser beams. Since the lasers fire at a rate of 10 Hz the vapor is repeatedly heated by many pulses.

During the C_{60} measurements, the ablation target had been removed and its support on the back flange was replaced by a Brewster window to allow the laser pulses to escape the furnace without ablating anything inside the tube. The beam was intercepted externally by an aluminum beam block located ~ 1 m from the end of the tube. See Fig. 1.

The current configuration uses two 10 Hz pulsed lasers (300 mJ/pulse and 5 mm in beam diameter), one operating at 532 nm (green), followed 50 ns later by the second one operating at 1064 nm (IR). Light emitted from the irradiated vapor is collected by an optical fiber placed at the focal point of a collecting lens. The collection is then from parallel rays having a collection diameter of ~ 10 mm. The fiber transfers the light to a Spex 270 M spectrograph having a gateable ICCD detector. The light is dispersed by a 300 line/mm grating blazed at 500 nm. All the spectra are intensity calibrated using a standard tungsten lamp with NIST traceable calibration. Time averaged spectra are collected with various gate widths and at different delay times after the laser pulse.

Transient spectral data are collected by a photomultiplier tube (PMT) connected to a transient digitizer having a 10 ns channel width. A 1 mm diameter region is focused on the PMT using a lens and pinhole. An IR blocking filter (KG-5) was used for all measurements. In addition, a notch filter (to remove the 532 nm laser line) and an interference filter centered at 510 nm with 10 nm bandpass were used for some measurements to select the $\Delta v = 0$ peak in the Swan band emission.

3. Results and discussion

A number of sets of transient and spectral measurements of radiation emitted from the laser-irradiated zone of the mixture of argon and C_{60} vapor were made at various conditions of oven temperature and background pressure. The partial pressure of C_{60} is determined by the oven temperature. The quartz tube was evacuated to a pressure of ~ 1 Pa and flushed with argon before maintaining an argon flow of 100 sccm at a pressure of 66.7 kPa. The oven is then heated slowly to 973 K, thus vaporizing some C_{60} from the vial. From a figure in Ref. [12], at 973 K the vapor pressure of C_{60} is estimated to be ~ 50 Pa, and its density is $\sim 10^{15}$ cm^{-3}, assuming the vapor is in equilibrium with the solid phase. Therefore, the maximum concentration of C_{60} is ~ 1 ppt.

3.1. Radiation measurements

To obtain time-dependent intensities of the emission a 1 mm diameter zone of laser irradiated C_{60} vapor at the center of the flow tube is imaged (1:1) on a photomultiplier tube (PMT). Its output is processed by a Le Croy transient digitizer with 10 ns bin width. One thousand scans are averaged. A small zero offset is subtracted before the data are plotted and analyzed. Time zero is taken as the laser Q-switch trigger. As seen in Fig. 2 emission from the zone peaks very rapidly, sometimes saturating the PMT circuitry at the peak. The emission decreases rapidly for ~ 2 μs, followed by a slower falloff lasting beyond 20 μs. Shoulders noted in the early part of the decay are attenuated with the 510 nm filter which transmits the $\Delta v = 0$ band of C_2 Swan system. During early times, the C_2 shows a decay time of ~ 300 ns (compared to a radiative lifetime of 100 ns for C_2 Swan bands). Later, beyond 3 μs, the decay time is much longer, on the order of 5 μs. The decay-time results are summarized in Table 1. The differences in decay time for the full spectrum (no filter) with temperature are probably real, but it is difficult to say what the trend is. Obviously, at higher temperatures there should be much more C_{60} in the laser path due to its higher vapor pressure. Also, its internal energy is larger, making it somewhat easier to dissociate.

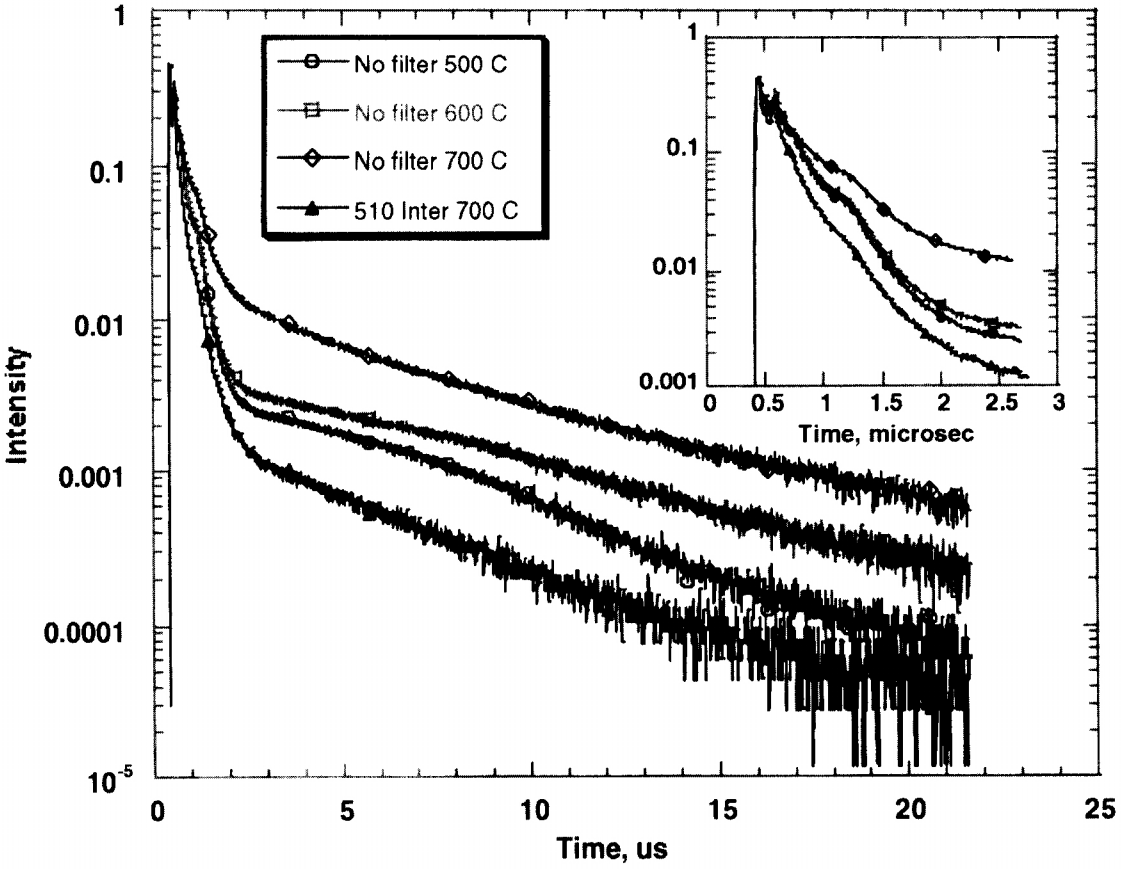

Fig. 2. Transient spectra with no filter of irradiated region at 773, 873 and 973 K, and at 973 K with 510 nm narrow band pass filter.

If the decay of C_2 Swan bands is a measure of dissociation from fullerenes then our decay time of 5 μs is about six times shorter than the decay time of C_{60} excited with 15 mJ/cm^2 at 193 nm observed by O'Brien et al. [4] (30 μs). Their condition is quite different from ours. Our fluence is 100 times higher, and the exciting photon energies are 2.8 and 5.5 times lower (green and IR, respectively). Apparently, the net effect in our experiment is greater excitation of C_{60}.

Spectral details of the radiation zone are recorded by collecting emission from a zone of ~ 10 mm in diameter using the fiber optic assembly located on the other side of the oven (Fig. 1). The spectrum is

Table 1
Summary of radiation decay times from laser irradiated C_{60}

Filter	Oven temp. (K)	Time interval (μs)	Decay time (μs)	Dominant radiation	Time interval (μs)	Decay time (μs)	Dominant radiation
None	500	4.0–21.5	4.8	C_2 Swan	0.7–1.7	0.303	black body
None	600	4.0–21.5	6.7	C_2 Swan	0.7–1.7	0.278	black body
None	700	5.2–21.6	6.4	C_2 Swan	0.56–1.86	0.452	black body
510	700	4.5–17.5	4.6	C_2 Swan	0.66–2.12	0.296	C_2 Swan

very weak; thus, we used a 500 μm entrance slit width. The resultant emission is similar to that obtained from the graphite target ablation during carbon nanotube production [1] and mostly contains C_2 Swan bands, but with faster decay times (5 μs compared with 20 μs). The spectrum taken in the interval of 0.5–1.0 μs (to 10 μs in the IR case) is shown in Fig. 3. The spectral features at 355 and 395 nm are from the aluminum plasma from the beam block. Scattered laser radiation at 532 nm is also seen. The dependence of spectral features on the laser wavelength is noted in Fig. 3, which clearly shows the major role of 532 nm laser beam in the production of C_2 from C_{60}. When only the IR laser (1064 nm) irradiates the C_{60} vapor no Swan band emission is seen. With only the green laser (532 nm), Swan band emission is seen; but with the IR laser following the green by 50 ns, the emission is increased ~ 50%, indicating that IR may contribute to excitation of C_{60} or daughter molecules. Another possibility is that the IR beam contributes to vaporizing graphite or amorphous carbon particles and freeing up fullerene clusters to be excited by next pulse of the green laser 100 ms later.

The recorded spectra at different delay times (0.5, 1, 10, 50 μs) from the laser trigger are shown in Fig. 4. The changes in relative intensity with time seem to indicate increasing vibrational temperatures. Estimates of the temperature were determined by comparing normalized measured spectra with calculated spectra at various temperatures. The 'best' visual fit yielded temperatures given in Table 2. It should be noted that these temperature estimates assume that the population of vibrational states is in a Boltzmann distribution. The intensity of the C_2 spectrum seems to decrease by two orders of magni-

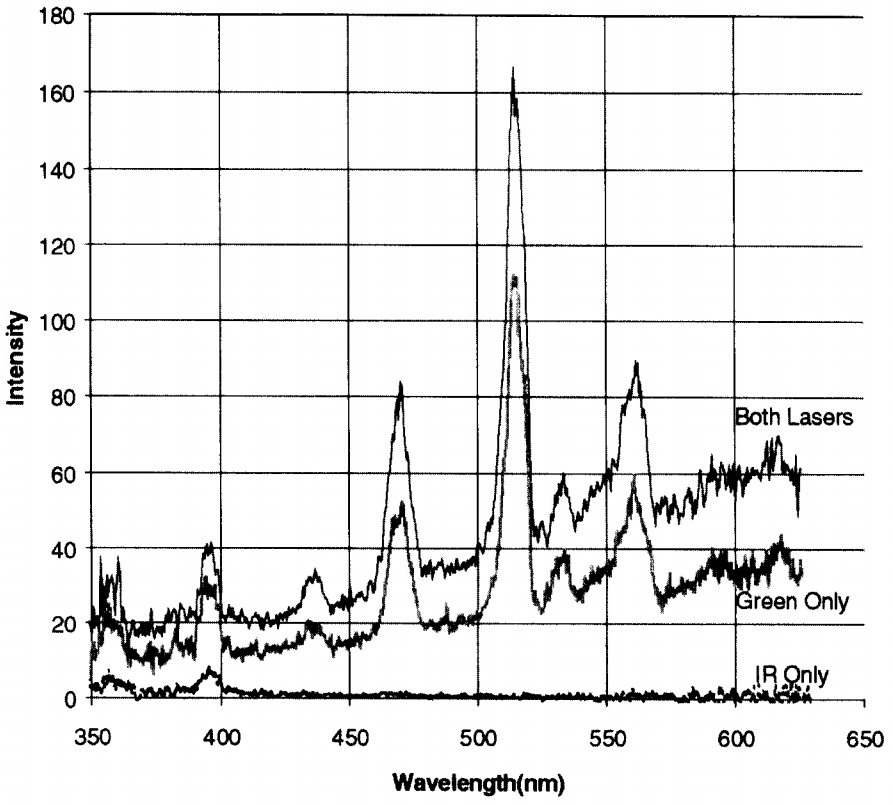

Fig. 3. Comparison of spectra taken 500 ns after different laser excitations. The spectral features at 355 and 395 nm are from aluminum plasma from the beam block. Scattered 532 nm is also seen.

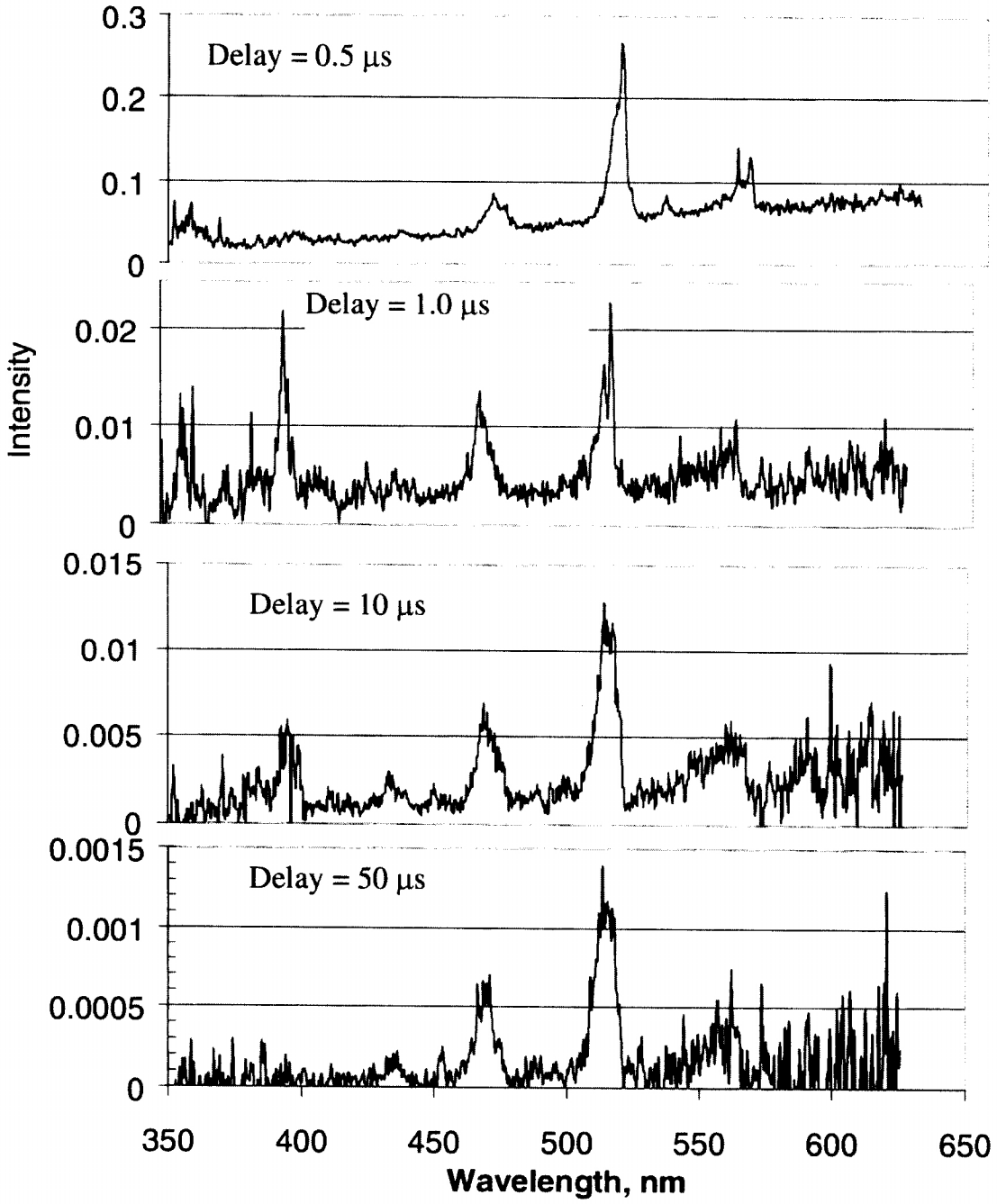

Fig. 4. Spectra acquired at delay times of 0.5, 1, 10, and 50 μs, showing C_2 Swan band peaks at all delay times. Note the increasing background continuum with increasing wavelength suggestive of black-body-type radiation.

tude within 50 μs. On the other hand, in the transient data of Fig. 2, one can note a decrease of three orders of magnitude. This difference is understood by the fact that the spatial resolution for the transient

Table 2
Estimated temperature of C_2 Swan band radiation at various delay times

Time (μs)	Temperature (K)
0.5	2000 ± 200
1.0	3000 ± 400
10	3000 ± 400
50	3500 ± 500

study is 1 mm; whereas, it is ~ 10 mm for the fiber optic spectra collection which averages the overall radiation in space as well as time in the radiation zone.

At the earliest measured time (500 ns delay) the spectrum has a significant continuum component underlying the C_2 spectrum. It is apparent that the source of the continuum cools very rapidly, or at least its intensity decreased to negligible values. The continuum could be from carbon particles, including fullerenes. To estimate the mean temperature of the particles during the early time of 0.5–1.0 μs we compared measured spectra and calculated black-body spectra for several temperatures as shown in Fig. 5. The black-body temperature that best matched the measurement is 3600 ± 200 K, which is higher than the C_2 vibrational temperature of 2000 ± 200 K estimated from the Swan bands. Since the intensity

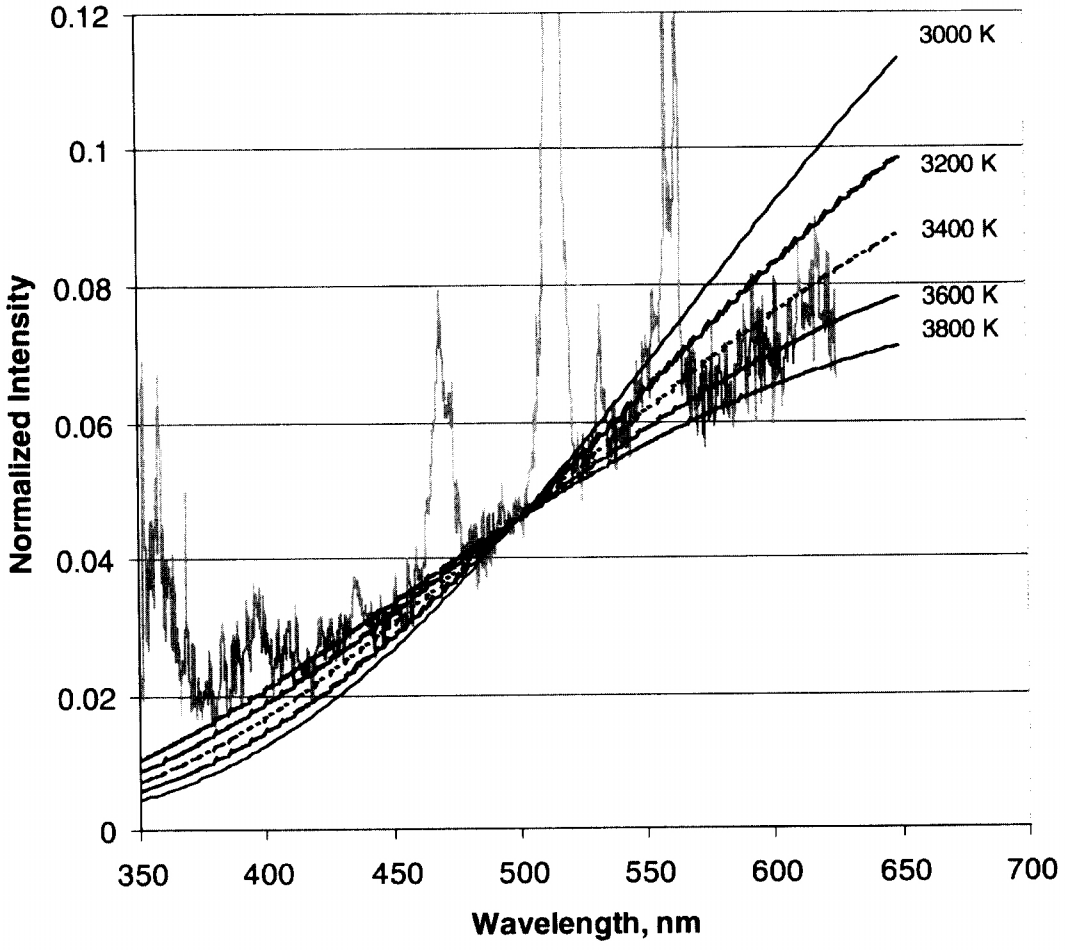

Fig. 5. Spectrum acquired at a delay time of 0.5 μs and a gate width of with black-body background compared with calculated normalized black-body spectra at several temperatures.

decays very rapidly, the average temperatures are weighted toward early times. Highly excited fullerene molecules may be at an internal temperature equivalent to several thousand kelvin [6]. According to Wurz and Lykke's work (Fig. 12 of Ref. [6]) a characteristic temperature of 3600 K would represent an internal energy of C_{60} of ~ 30 eV compared to the 2.33 eV photon energy of the 532 nm beam.

The laser energy per pulse of 0.3 J represents an average fluence $F = 1.53$ J/cm^2 over the beam diameter. The fluence of 532 nm photons (energy 2.33 eV) is then $F_n = F/h\nu = 4 \times 10^{18}$ cm.

The cross-section for excitation $\sigma = 1.86 \times 10^{-18}$ is obtained from ratio of absorption data of Ref. [13] and from cross-section data at 973 K and 238 nm from Ref. [14]. We estimate the number of excitations per pulse to be $\sigma F_n = 7$ per molecule of C_{60}, which corresponds to an excitation of ~ 16 eV. The number is larger in the center of the beam where its intensity is peaked. There is quite a bit of disagreement about the energy required to eject a C_2 from C_{60}. However, if we assume a value of 11.6 eV [15], plus a mean excitation energy of 3 eV to excite the C_2 to the $d^3\Pi_g$ state, we would require only 6.3 photons of 532 nm light. At 973 K C_{60} already has ~ 6 eV of internal energy [6] and the excess energy from the multiphoton absorption can, therefore, excite C_{60} and its daughters sufficiently to eject C_2 in electronically excited states. The energetics can also explain lack of C_2 Swan band emission with only the IR laser excitation. A high level of excitation would lead to temperatures at least as high as measured from the continuum radiation at early times.

Based on ratio of intensities of C_2 Swan band peak emission its estimated vibrational temperature increases from 2000 to 3500 K with time. This may be due to some sort of incubation or rearrangement of energy in the fullerene that leads to greater excitation of C_2. The persistence of Swan band emission could stem from the rate constant of C_{60} unimolecular decay and from dissociation of fullerene decay products during a 'shrink wrap' process. It is not possible to determine which process from our experiments. Lack of Swan band emission when C_{60} is irradiated by the IR laser probably results from the smaller photon absorption cross-section at that wavelength and lack of sufficient energy to produce excited C_2 from any photodissociated C_{60}.

Other means of producing excited C_2 are possible. Multi-pulse excitation of dissociation products is possible under our current slow flow conditions. Atomic carbon can recombine to form C_2 in the $d^3\Pi_g$-state. Whereas atomic carbon may be a dissociation product of photodissociation of fullerenes, it is not formed in nearly as large quantities as C_2 [16]. Atomic carbon may also be produced by the exchange reaction

$$C_2 + C_2 \rightarrow C_3 + C,$$

since the forward reaction is energetically favorable. However, the intensity of C_2 Swan band emission was estimated to be much smaller than observed in our experiment, based on the rate of this reaction and the subsequent atom recombination reaction

$$C + C \rightarrow C_2^* .$$

Unimolecular ionization of excited C_{60} is also possible, leading to the possibility that electrons could excite C_2. However, ion recombination at these low temperatures and relatively high pressure will assure that electrons will disappear very quickly and their energies will probably be too low to excite C_2 to radiative states. Therefore, we conclude that the observed C_2 Swan band emission may be due to C_2 ejected in its excited $d^3\Pi_g$-state from C_{60} and/or its daughter fullerenes, C_{58}, C_{56}, etc.

4. Conclusions

Vapor of the fullerene C_{60} at 973 K was irradiated by two laser pulses operated at a fluence of ~ 1.5 J/cm^2 per pulse. Measurements were made of the emission from the region to obtain transient decay of wide and narrow spectral bands. Spectra covering ~ 400–675 nm were also measured in the region. The main radiation observed was C_2 Swan bands, and at early times, a black-body continuum having an estimated temperature of 3600 K. Swan band emission of C_2 continues for at least 50 μs from early times, indicating that production of C_2 persists for a long period of time compared to its radiative lifetime.

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